Derivation of Soil PAH Cleanup Goals Using the Multimed Model

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ABSTRACT

Soil cleanup levels for a source area of chemical release that are protective of groundwater at some downgradient receptor location can be predicted through the application of U.S. EPA's recently developed Multimedia Exposure Assessment Model (Multimed). This computer model was instrumental as part of an FS in modeling the unsaturated and saturated zone fate and transport of total polycyclic aromatic hydrocarbons (total PAHs). This FS is being conducted at an inactive wood treating facility that is currently listed as a Superfund site.

Groundwater investigations revealed the potential for PAHs to leach from source soils located in two Areas at the site, designated A and B, and to migrate horizontally through the underlying aquifer to a downgradient well location and an adjacent estuarine river, respectively. This prompted the U.S. EPA to recommend development of soil cleanup goals using Multimed that were protective of: (1) humans consuming groundwater at the receptor well location impacted by Area A, (2) organisms inhabiting the river, and (3) humans consuming organisms from the river impacted by Area B.

Deterministic and Monte Carlo steady-state chemical transport simulations were performed by coupling the unsaturated and saturated zone modules of Multimed to determine downgradient groundwater concentrations at each the receptor location. Input values for source-specific, aquifer-specific, and chemical-specific variables determined the degree to which PAHs were diluted and attenuated due to the simulated effects of infiltration into the aquifer, three-dimensional dispersion, and linear adsorption.

Dilution-attenuation factors (DAFs) were calculated for total PAHs by dividing the initial leachate concentrations of total PAHs at the source by the downgradient output concentrations derived by Multimed. Multiplication of applicable and appropriate performance standards by the DAFs resulted in the soil leachate concentrations of total PAHs at the source locations. A partitioning equation was applied to the leachate concentrations to derive soil cleanup concentrations of total PAHs.

The soil cleanup goals for total PAHs in Area A, derived from the results of the deterministic and Monte Carlo simulations, for protection of the humans consuming groundwater at the receptor well location were 2,738 mg/kg and 10,355 mg/kg, respectively. The soil cleanup goals for total PAHs in Area B, derived from the results of the deterministic and Monte Carlo simulations, for protection of the humans consuming river organisms were 41,866 mg/kg and 35,067 mg/kg, respectively. The soil cleanup goals for total PAHs in Area B, derived from the results of the deterministic and Monte Carlo simulations, for protection of river organisms were both greater than 1,000,000 ppm. Based on these soil cleanup goals and the existing PAH concentrations detected at the site, no soil remediation of PAHs would be necessary in either Area A or B.

INTRODUCTION

An RI/FS is currently being conducted at a former wood treating/storage facility in Virginia, that is currently listed on the NPL. The developmental process of the RI/FS for the site is being supervised by the U.S. EPA's the Region 3 and the Virginia Department of Waste Management (VDWM).

A Final RI Report, which characterized the nature and extent of contamination of surface and subsurface soils at the site as well as groundwater in the shallow, unconfined Columbia and the deep Yorktown aquifers beneath the site, was submitted to the U.S. EPA and VDWM and subsequently approved. Analytical groundwater data acquired for the shallow, unconfined aquifer during the RI revealed that detectable concentrations of polycyclic aromatic hydrocarbons (PAHs) were present in the groundwater. Analytical data acquired during the RI also revealed the presence of the same PAHs in the unsaturated zone soils above the shallow aquifer. Both potentially carcinogenic and noncarcinogenic PAHs (cPAHs and nPAHs, respectively), which are commonly associated with wood treating/storage activities, were identified as contaminants in a Public Health and Environmental Assessment (PHEA) that was performed as part of the Final RI for the site (Table 1).

Two areas, Area A and Area B, were delineated as potential source areas on the western and eastern portions of the site, respectively (Figure 1). The presence of PAHs in the soil and groundwater samples collected from these areas implies the possibility of downward vertical movement of organic leachate from the unsaturated zone to the groundwater of the Columbia Aquifer. Once in the groundwater, the potential exists for the transport of PAHs from beneath source Areas A and B to a receptor domestic well and an adjacent estuarine river, respectively. Although the aquifer is not currently being used as a potable water supply, it could be used as such in the future. Hypothetical domestic wells are therefore considered to be potential receptors in a future scenario. The adjacent river is considered to be a potential environmental receptor for those PAHs which have leached from the soil into the shallow aquifer at the site.

For the purposes of conducting a focused FS, it became necessary to develop soil cleanup goals for PAHs that were protective of: (1) humans consuming groundwater at a receptor well location impacted by Area A, (2) organisms inhabiting the river, and (3) humans consuming organisms from the river impacted by Area B. The U.S. EPA suggested that this task be performed by applying the U.S. EPA's Multimedia Exposure Assessment Model (Multimed) to designated source area(s) at the site.[1]

The monitoring well designated MW-102 (Figure 1), installed in the Columbia aquifer in the southwestern portion of the site, was selected as the receptor well location for PAHs migrating from Area A since it is situated downgradient of source Area A and PAHs were detected in groundwater samples collected from this location. In addition, it is more likely that property west of the site may undergo residential development, rather than any other on-site or off-site location. The adjacent river, as stated previously, was determined to be the potential environmental receptor for constituents migrating from source Area B.

The purpose of Multimed in the development of soil cleanup goals was the derivation of dilution-attenuation factors (DAFs) that are used as multipliers for selected applicable and appropriate performance standards at the receptor of interest.

Table 1
Summary of Polycyclic Aromatic Hydrocarbons (PAHs) Detected in Soil and Groundwater Samples During Remedial Investigation

2-Methylnaphthalene
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzofuran
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
2-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene

DESCRIPTION OF MULTIMED

Multimed is a recently developed user-friendly model that is capable of simulating chemical release, in leachate form, from a source (or designated area) at the site to soils directly beneath the source. In addition, Multimed can be used to further simulate chemical fate and transport in the unsaturated and saturated zones followed by possible interception of the subsurface plume by a specified receptor (e.g., a well or surface stream).

The fate and transport of a chemical released from a source is simulated in Multimed by incorporating the known responses of the chemical to a number of complex physical, chemical, and biological processes the chemical encounters as it moves in the multimedia environment. These responses are incorporated as chemical-specific variable input data by the model user. Other variable input data, such as source-specific and aquifer-specific data, must also be incorporated by the user. For some of the variable input data, the model provides the user with an option to either (1) manually specify values for the variable input data (constant input) or (2) have the model mathematically derive the variable input data from other constant input (derived input).

After all relevant input data have been defined and the type of output desired has been specified, the multimedia transport of each contaminant is mathematically simulated by the model. An output file is then generated showing final concentrations of specific constituents and any other pertinent information (i.e., times of concentration occurrences or statistical distributions resulting from multiple iterations). The final downgradient concentration(s) produced by the model can be used to represent potential toxic exposure concentration(s) that may occur to human and/or environmental receptors.

For this site, deterministic and Monte Carlo simulations of steady-state unsaturated and saturated zone flow and transport were performed using Multimed. A gaussian boundary condition was applied to the saturated zone transport of the contaminants away from the source, with the maximum concentration occurring at the source.

Steady-state conditions in the model were used for the approximation of a system mass balance in which water entering the flow system is balanced by the water leaving the system. There is no significant temporal variation in the system. Thus, the assumption of a steady-state system basically simplifies the mathematical equations used to describe the flow and transport processes and reduces the amount of input data since no information on temporal variability is necessary.

The assumption of steady-state flow and transport requires that the source be of sufficiently large mass to ensure that the final downgradient contaminant concentration in the groundwater is maintained at the receptor location. The source is assumed to be continuous and constant, without decay or any other temporal variation.

In the deterministic model of steady-state conditions, each input variable is of fixed value and is assumed to have a fixed mathematical relationship with the other variables. Each run of a deterministic model can result in either the output of one maximum concentration or time-stepped concentrations occurring over a specified time interval. For this site, the output selected was the maximum concentration that would occur over an arbitrarily selected 500-year period.

The deterministic mode of the Multimed model should only be applied to a particular modeling situation(s) in which all values for the input variables are known, or can be assumed with a high level of confidence. If uncertainty in the values of input variables exists, then the simulation(s) may be performed within the Monte Carlo framework, where the randomness and uncertainties of values inherent with the modeled system can be evaluated. Input values in the deterministic model were either constant or derived values. Tables 2 through 4 present all values used in defining the unsaturated and saturated zone input variable parameters assumed for the site in the deterministic model.

The Monte Carlo method provided a means of applying the known uncertainty associated with an input variable to that variable. This uncertainty is expressed as a cumulative probability distribution. For each uncertain input variable, a probability distribution must be specified that best describes the frequencies of occurrences of measured values for that variable. As the Monte Carlo simulation is run over a large number of iterations (the number of iterations is specified by the user), random values generated from a specified probability distribution are assigned to the variable. For this site, 500 Monte Carlo simulations were performed by Multimed. The probability distribution may be specified as uniform, log10 uniform, normal, log10 normal, exponential, empirical, or the Johnson System of distributions. Relating the input variable to any one cumulative probability distribution may be difficult. The difficulty arises from the fact that the specification of a distribution for an input variable requires a large amount of site-specific data on that variable that may not be available.

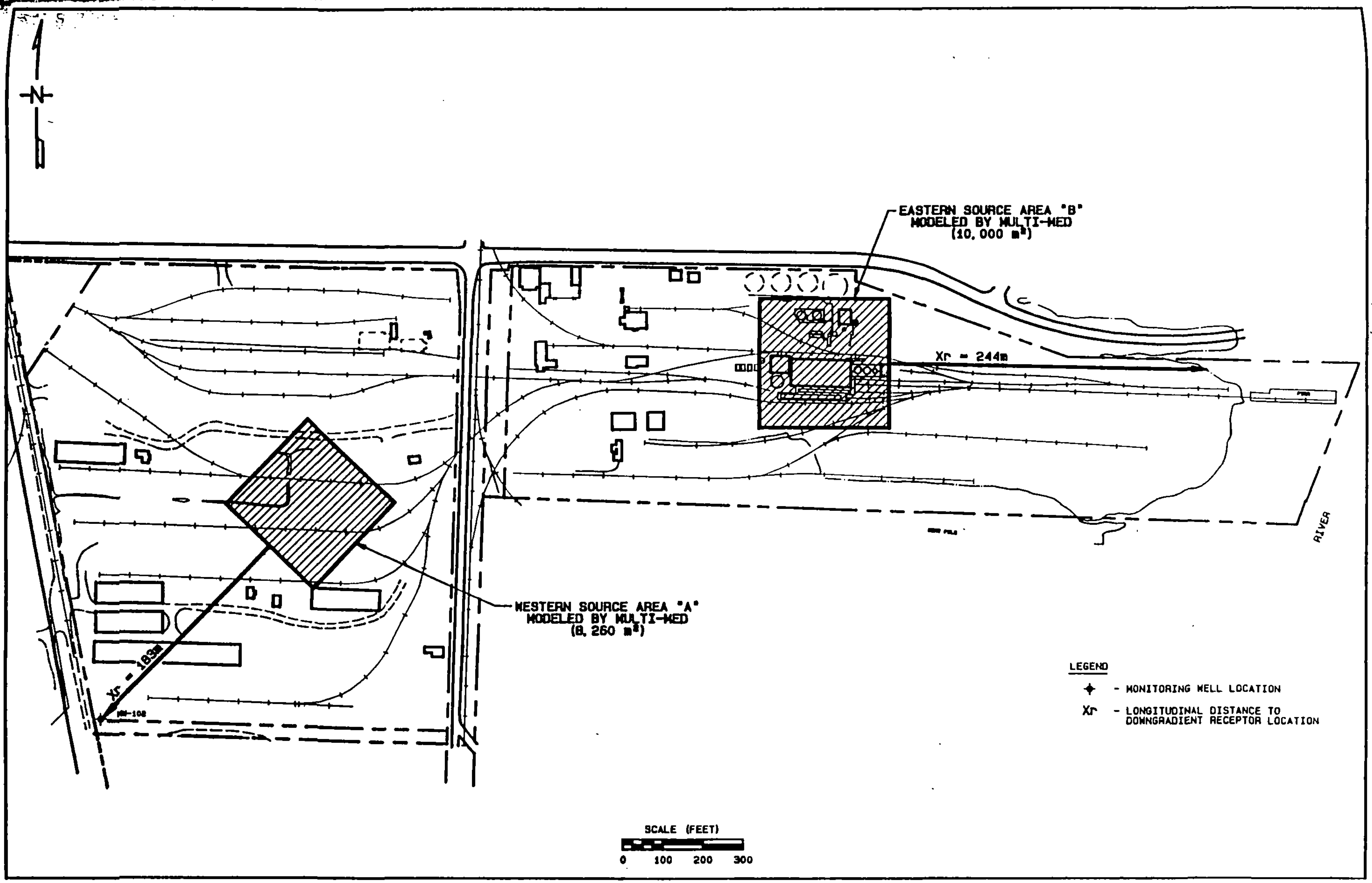

Figure 1
Source Areas Modeled by U.S. EPA
Exposure Assessment Multimedia Model

Table 2
Summary of Mutilated Input Parameters Used in Modeling PAH
Leachate Flow and Transport Through the
Unsaturated Zone for Modeling to MW-102 and the River
Deterministic Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE	INPUT TYPE	COMMENTS
UNSATURATED ZONE MATERIAL VARIABLES				
Depth of Unsaturated Zone	m	1	CONSTANT	—
Number of Layers	—	1	CONSTANT	—
Saturated Hydraulic Conductivity	cm/hr	4.42	CONSTANT	(a)
Unsaturated Zone Porosity	—	0.38	CONSTANT	(b)
UNSATURATED ZONE FUNCTION VARIABLES				
ALFA Coefficient	1/cm	0.075	CONSTANT	(c)
Residual Water Content	—	0.065	CONSTANT	(d)
Van Genuchten Exponent	—	1.89	CONSTANT	(c)
UNSATURATED ZONE TRANSPORT VARIABLES				
Bulk Density of Soil for Layer	g/cc	1.49	CONSTANT	(e)
Longitudinal Dispersivity of Layer	m	0.042	DERIVED	(f)
Percent Organic Matter	—	0.5	CONSTANT	(g)
Thickness of Layer	m	1	CONSTANT	—

NOTES:

(a) Literature value obtained from Multimed User's Manual (1), Table 6–2, for sandy loam.

(b) Value obtained from Multimed User's Manual (1), Table 6–3. Represents average porosity for sand (fine and coarse), gravel (fine and coarse), silt, and clay.

(c) Literature value obtained from Multimed User's Manual (1), Table 6–5, for sandy loam.

(d) Literature value obtained from Multimed User's Manual (1), Table 6–4, for sandy loam.

(e) Literature value obtained from Multimed User's Manual (1), Table 6–8, for sandy loam.

(f) Value obtained from the following calculation:

$av = 0.02 + 0.022L,$

where av = longitudinal dispersivity (unsaturated flow in the vertical direction)

L = depth of the unsaturated zone = 1m

(g) Literature obtained from Multimed User's Manual (1), Table 6–7, for Group B soils.

Table 3
Summary of Mutilated Input Parameters Used in Modeling PAH
Leachate Flow and Transport Through the Saturated Zone
of the Columbia Aquifer to Receptor Well Location MW-102
Deterministic Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE	INPUT TYPE	COMMENTS
CHEMICAL-SPECIFIC VARIABLES				
Acid Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Base Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Biodegradation Coefficient (Sat. Zone)	1/yr	0	CONSTANT	(a)
Dissolved Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
Distribution Coefficient, Kd	—	—	DERIVED	(b)
Neutral Hydrolysis Rate Constant	1/yr	0	CONSTANT	(a)
Normalized Distribution Coefficient, Koc	ml/g	—	CONSTANT	(a)
Overall Chemical Decay Coefficient	1/yr	0	CONSTANT	(c)
Overall First-Order Decay Coefficient	1/yr	0	DERIVED	(d)
Reference Temperature	C	25	CONSTANT	(e)
Solid Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
SOURCE-SPECIFIC VARIABLES				
Area of Western Source	sq.m.	8,260	CONSTANT	(f)
Duration of Pulse	yr	—	CONSTANT	(e)
Infiltration Rate	m/yr	0.317	CONSTANT	(g)
Initial Concentration of Leachate	mg/L	100	CONSTANT	(h)
Length Scale of Source	m	90.88	DERIVED	(f)
Near Field Dilution	—	>1	DERIVED	(g)
Recharge Rate	m/yr	0.317	CONSTANT	(g)
Source Decay Constant	1/yr	0	CONSTANT	(c)
Spread of Contaminant Source	m	15.1	DERIVED	(i)
Width Scale of Source	m	90.88	DERIVED	(f)
AQUIFER-SPECIFIC VARIABLES				
Angle off Centerline of Plume	degree	0	CONSTANT	(e)
Aquifer Porosity	—	0.38	CONSTANT	(j)
Aquifer Thickness	m	5.34	CONSTANT	—
Bulk Density	g/cc	1.49	CONSTANT	(k)
Distance to Receptor, Xr	m	183	CONSTANT	(l)
Groundwater Seepage Velocity	m/yr	—	DERIVED	(m)
Hydraulic Conductivity	m/yr	442	CONSTANT	—
Hydraulic Gradient	—	0.006	CONSTANT	—
Longitudinal Dispersivity	m	18.3	CONSTANT	(n)
Mixing Zone Depth	m	—	DERIVED	(m)
Organic Carbon Content (Fraction), foc	—	0.005	CONSTANT	(o)
Particle Diameter	cm	0.03	CONSTANT	(p)
Retardation Coefficient	—	—	DERIVED	(q)
Temperature of Aquifer	C	18	CONSTANT	(e)
Transverse Dispersivity	m	6.1	CONSTANT	(n)
Vertical Dispersivity	m	1.02	CONSTANT	(n)
pH	—	6.5	CONSTANT	(e)

NOTES FOR TABLE 3

(a) Literature value obtained from Aquatic Fate Process Data for Organic Priority Pollutants (4).

(b) Distribution coefficient (not presented by model output) was derived from the following calculation:
Kd = Koc * foc,
where Koc = normalized distribution coefficient
foc = organic carbon content (fraction)

(c) Conservative input value assumed.

(d) Value will be zero since it is derived from solid and dissolved phase coefficients, which themselves were assigned a value of zero.

(e) Temporal factors are ignored under steady-state conditions.

Area was designated as shown in Figure 1. Model assumed area is square, approximated area at 8,260 sq.m. with length = width = 90.88 m.

(g) Infiltration and recharge rates selected for model represents minimum value derived from Hydrological Evaluation of Landfill Performance (HELP) model.

(h) Assumed value.

(i) Spread of gaussian contaminant source = width of source/6.

(j) Value represents mean of the mean porosity values for materials ranging from fine sand to clay - Table 6-3, Multimed User's Manual (1).

(k) Literature value obtained from Multimed User's Manual (1), Table 6-8, for sandy loam.

(l) Determined from Figure 1.

(m) Model-derived value unknown to user.

(n) Longitudinal Dispersivity, aL = 0.1*Xr
Transverse Dispersivity = aL/3
Vertical Dispersivity = 0.056*aL

(o) No site-specific foc data available. Input value of 0.005 is a model default value which falls within range of foc values derived from fom values obtained from Multimed User's Manual (1), Table 6-7, for Group B soils using the following equation:
foc = fom/172.4.

(p) Mean particle diameter assumed from range given for medium sand in Table 6-10 of Multimed User's Manual (1).

(q) Actual model-derived Rd value unknown to user.

Table 4
Summary of Mutilated Input Parameters Used in Modeling PAH Leachate Flow and Transport Through the Saturated Zone of the Columbia Aquifer to the Adjacent River Deterministic Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE	INPUT TYPE	COMMENTS
CHEMICAL-SPECIFIC VARIABLES				
Acid Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Base Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Biodegradation Coefficient (Sat. Zone)	1/yr	0	CONSTANT	(a)
Dissolved Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
Distribution Coefficient, Kd	—	—	DERIVED	(b)
Neutral Hydrolysis Rate Constant	1/yr	0	CONSTANT	(a)
Normalized Distribution Coefficient, Koc	ml/g	—	CONSTANT	(a)
Overall Chemical Decay Coefficient	1/yr	0	CONSTANT	(c)
Overall First-Order Decay Coefficient	1/yr	0	DERIVED	(d)
Reference Temperature	C	25	CONSTANT	(e)
Solid Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
SOURCE-SPECIFIC VARIABLES				
Area of Eastern Source	sq.m.	10,000	CONSTANT	(f)
Duration of Pulse	yr	—	CONSTANT	(e)
Infiltration Rate	m/yr	0.317	CONSTANT	(g)
Initial Concentration of Leachate	mg/L	100	CONSTANT	(h)
Length Scale of Source	m	100	DERIVED	(f)
Near Field Dilution	—	>1	DERIVED	(g)
Recharge Rate	m/yr	0.317	CONSTANT	(g)
Source Decay Constant	1/yr	0	CONSTANT	(c)
Spread of Contaminant Source	m	16.7	DERIVED	(i)
Width Scale of Source	m	100	DERIVED	(f)
AQUIFER-SPECIFIC VARIABLES				
Angle off Centerline of Plume	degree	0	CONSTANT	(e)
Aquifer Porosity	—	0.38	CONSTANT	(j)
Aquifer Thickness	m	5.34	CONSTANT	—
Bulk Density	g/cc	1.49	CONSTANT	(k)
Distance to Receptor, Xr	m	244	CONSTANT	(l)
Groundwater Seepage Velocity	m/yr	—	DERIVED	(m)
Hydraulic Conductivity	m/yr	820	CONSTANT	—
Hydraulic Gradient	—	0.006	CONSTANT	—
Longitudinal Dispersivity	m	24.4	CONSTANT	(n)
Mixing Zone Depth	m	—	DERIVED	(m)
Organic Carbon Content (Fraction), foc	—	0.005	CONSTANT	(o)
Particle Diameter	cm	0.03	CONSTANT	(p)
Retardation Coefficient	—	—	DERIVED	(q)
Temperature of Aquifer	C	18	CONSTANT	(e)
Transverse Dispersivity	m	8.13	CONSTANT	(n)
Vertical Dispersivity	m	1.37	CONSTANT	(n)
pH	—	6.5	CONSTANT	(e)

NOTES FOR TABLE 4:

(a) Literature value obtained from Aquatic Fate Process Data for Organic Priority Pollutants (4).

(b) Distribution coefficient (not presented by model output) was derived from the following calculation:
Kd = Koc * foc,
where Koc = normalized distribution coefficient
foc = organic carbon content (fraction)

(c) Conservative input value assumed.

(d) Value will be zero since it is derived from solid and dissolved phase coefficients, which themselves were assigned a value of zero.

(e) Temporal factors are ignored under steady-state conditions.

(f) Area was designated as shown in Figure 1. Model assumed area is square, approximated area at 10,000 sq.m. with length = width = 100 m.

(g) Infiltration and recharge rates selected for model represents minimum value derived from Hydrological Evaluation of Landfill Performance (HELP) model.

(h) Assumed value.

(i) Spread of gaussian contaminant source = width of source/6.

(j) Value represents mean of the mean porosity values for materials ranging from fine sand to clay - Table 6-3, Multimed User's Manual (1).

(k) Literature value obtained from Multimed User's Manual (1), Table 6-8, for sandy loam.

(l) Determined from Figure 1.

(m) Model-derived value unknown to user.

(n) Longitudinal Dispersivity, aL = 0.1*Xr
Transverse Dispersivity = aL/3
Vertical Dispersivity = 0.056*aL

(o) No site-specific foc data available. Input value of 0.005 is a model default value which falls within range of foc values derived from fom values obtained from Multimed User's Manual (1), Table 6-7, for Group B soils using the following equation:
foc = fom/172.4.

(p) Mean particle diameter assumed from range given for medium sand in Table 6-10 of Multimed User's Manual (1).

(q) Actual model-derived Rd value unknown to user.

The types of values assigned to the Monte Carlo, steady-state input variables were either constant, derived, or ranges of uniform distribution. For this site, a uniform distribution of values was specified for each select input variable due to the lack of site-specific data for those variables. All values used to define the unsaturated and saturated zone input variable parameters assumed for the site in the Monte Carlo, steady-state model are presented in Tables 5 through 8.

USE OF OUTPUT DATA FOR DERIVATION OF SITE-SPECIFIC SOIL CLEANUP GOALS

As stated previously, the purpose of Multimed in the development of site-specific cleanup goals is the derivation of dilution-attenuation factors. These derived factors are then used as multipliers for selected performance standards at the receptor locations of interest. Rather than developing soil cleanup levels for each PAH compound individually, one soil cleanup goal for total PAHs was calculated that will be protective of the groundwater at monitoring well MW-102, marine organisms in the river, and humans consuming organisms from the river.

The groundwater performance standard assumed at well location MW-102 for the derivation of an soil cleanup goal for total PAHs at Area A was the proposed maximum contaminant level (MCL) for benzo(a)anthracene, 0.0001 mg/L.[2] Although there are various MCLs and DWELs established for the individual PAH compounds, this MCL was selected for the total PAHs since it represents the most conservative drinking water standard. The performance standards assumed at the river for the derivation of soil cleanup goals for total PAHs that were protective of marine organisms and humans consuming organisms from the river impacted by Area B were 0.3 mg/L[3] and 0.0000311 mg/L,[3] respectively.

Prior to discussing the actual calculation process, Table 9 presents and defines the parameters which were used in the development of soil cleanup goals.

Groundwater Approach

The calculations for developing soil cleanup goals protective of groundwater at the designated receptor well location MW-102 are as follows:

Table 5
Summary of Mutilated Input Parameters Used in Modeling PAH Leachate Flow and Transport Through the Saturated Zone for Modeling to MW-102 Monte Carlo Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE(S)	INPUT TYPE	COMMENTS
<u>UNSATURATED ZONE MATERIAL VARIABLES</u>				
Depth of Unsaturated Zone	m	0.613 - 1.33	UNIFORM	—
Number of Layers	—	1	CONSTANT	—
Saturated Hydraulic Conductivity	cm/hr	1.0 - 150	UNIFORM	—
Unsaturated Zone Porosity	—	0.250 - 0.500	UNIFORM	—
<u>UNSATURATED ZONE FUNCTION VARIABLES</u>				
ALFA Coefficient	1/cm	0.005 - 0.145	UNIFORM	(a)
Residual Water Content	—	0.034 - 0.100	UNIFORM	(b)
Van Genuchten Exponent	—	1.09 - 2.68	UNIFORM	(a)
<u>UNSATURATED ZONE TRANSPORT VARIABLES</u>				
Bulk Density of Soil for Layer	g/cc	1.25 - 1.76	UNIFORM	(c)
Longitudinal Dispersivity of Layer	m	—	DERIVED	(d)
Percent Organic Matter	—	0.180 - 1.30	UNIFORM	(e)
Thickness of Layer	m	0.500 - 2.00	UNIFORM	(a)

<u>NOTES:</u>

(a) Literature values obtained from Multimed User's Manual (1), Table 6–5, for sandy loam.
(b) Literature values obtained from Multimed User's Manual (1), Table 6–4, for sandy loam.
(c) Literature values obtained from Multimed User's Manual (1), Table 6–8, for sandy loam.
(d) Derived values obtained from the following calculation:
$av = 0.02 + 0.022L$,
where av = longitudinal dispersivity (unsaturated flow in the vertical direction)
L = depth of the unsaturated zone = 1 m
(e) Literature values obtained from Multimed User's Manual (1), Table 6–7, for Group B soils.

- Initial PAH concentrations (C_i) are modeled from the designated source area through the unsaturated and saturated zones to the receptor location at monitoring well MW-102. A groundwater concentration at this location (C_r) is output by the model.
- The following relationship is then used to calculate a DAF:

$$DAF = C_i/C_r \quad (1)$$

- Assuming the target PAH groundwater concentration at location MW-102 to be C_{std}, multiplying C_{std} by the model-derived DAF (derived in the previous step 2) gives the PAH leachate concentration (C_l) at the source, or:

$$C_l = C_{std}\, DAF \quad (2)$$

- Finally, multiplication of C_l by the distribution coefficient (K_d) results in a soil concentration at the source corresponding to the soil cleanup goal. This partitioning is expressed as the following:

$$C_s = C_l\, K_d \quad (3)$$

Table 6
Summary of Mutilated Input Parameters Used in Modeling PAH Leachate Flow and Transport Through the Saturated Zone of the Columbia Aquifer to Receptor Well Location MW-102 Monte Carlo Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE(S)	INPUT TYPE	COMMENTS
CHEMICAL-SPECIFIC VARIABLES				
Acid Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Base Catalyzed Hydrolysis Rate	1/M-yr	0	CONSTANT	(a)
Biodegradation Coefficient (Sat. Zone)	1/yr	0	CONSTANT	(a)
Dissolved Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
Distribution Coefficient, Kd	—	—	DERIVED	(b)
Neutral Hydrolysis Rate Constant	1/yr	0	CONSTANT	(a)
Normalized Distribution Coefficient, Koc	ml/g	14.2 - 5,500,000	UNIFORM	(a)
Overall Chemical Decay Coefficient	1/yr	0	CONSTANT	(c)
Overall First-Order Decay Coefficient	1/yr	0	DERIVED	(d)
Reference Temperature	C	25	CONSTANT	(e)
Solid Phase Decay Coefficient	1/yr	0	CONSTANT	(a)
SOURCE-SPECIFIC VARIABLES				
Area of Western Source	sq.m.	8,260	CONSTANT	(f)
Infiltration Rate	m/yr	0.317 - 0.587	UNIFORM	(g)
Initial Concentration of Leachate	mg/L	100	CONSTANT	(h)
Length Scale of Source	m	90.88	DERIVED	(f)
Near Field Dilution	—	1	DERIVED	(g)
Recharge Rate	m/yr	0.308 - 0.744	UNIFORM	—
Source Decay Constant	1/yr	0	CONSTANT	(c)
Spread of Contaminant Source	m	15.1	DERIVED	(i)
Width Scale of Source	m	90.88	DERIVED	(f)
AQUIFER-SPECIFIC VARIABLES				
Angle off Centerline of Plume	degree	0	CONSTANT	(e)
Aquifer Porosity	—	0.26 - 0.57	UNIFORM	(j)
Aquifer Thickness	m	4.57 - 6.10	UNIFORM	—
Bulk Density	g/cc	1.25 - 1.76	UNIFORM	(k)
Distance to Receptor, Xr	m	183	CONSTANT	(l)
Groundwater Seepage Velocity	m/yr	—	DERIVED	—
Hydraulic Conductivity	m/yr	347 - 536	UNIFORM	—
Hydraulic Gradient	—	0.0011 - 0.0100	UNIFORM	—
Longitudinal Dispersivity	m	18.3	CONSTANT	(m)
Mixing Zone Depth	m	—	DERIVED	—
Organic Carbon Content (Fraction), foc	—	0.0010 - 0.0076	UNIFORM	(n)
Particle Diameter	cm	0.0004 - 0.2000	UNIFORM	(o)
Retardation Coefficient	—	—	DERIVED	—
Temperature of Aquifer	C	16 - 25	UNIFORM	(e)
Transverse Dispersivity	m	6.1	CONSTANT	(m)
Vertical Dispersivity	m	1.02	CONSTANT	(m)
pH	—	6.00 - 9.00	CONSTANT	(e)

NOTES FOR TABLE 6:

(a) Literature values obtained from Aquatic Fate Process Data for Organic Priority Pollutants (4).

(b) Distribution coefficient was derived from the following equation:
$Kd = Koc * foc$,
where Koc = normalized distribution coefficient
Foc = organic carbon content (fraction)

(c) Conservative input value assumed.

(d) Value will be zero since it is derived from solid and dissolved phase coefficients, which themselves were assigned a value of zero.

(e) Assumed value(s).

(f) Area was designated as in Figure 1. Model assumed area is square, approximated area at 8,260 sq.m., with length = width = 90.88 m.

(g) Infiltration rates selected for model represents the minimum and maximum values derived from the Hydrological Evaluation of Landfill Performance (HELP) model.

(h) Assumed value.

(i) Spread of gaussian contaminant source = width of source/6.

(j) Porosity values represent range from fine sand to clay – Table 6–3, Multimed User's Manual (1).

(k) Literature values obtained from Multimed User's Manual (1), Table 6–8, for sandy loam.

(l) Determined from Figure 1.

(m) Longitudinal Dispersivity, $aL = 0.1*Xr$
Transverse Dispersivity = $aL/3$
Vertical Dispersivity = $0.056*aL$

(n) No site–specific foc data available. Input value range obtained from Multimed User's Manual (1), Table 6–7, for Group B soils using the following equation:
$foc = fom/172.4$.

(o) Particle diameter range assumed for particle types ranging from fine silt to coarse gravel, given in Table 6–10 of the Multimed User's Manual (1).

Table 7
Summary of Mutilated Input Parameters Used in Modeling PAH Leachate Flow and Transport Through the Saturated Zone for Modeling to the Adjacent River
Monte Carlo Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE(S)	INPUT TYPE	COMMENTS
UNSATURATED ZONE MATERIAL VARIABLES				
Depth of Unsaturated Zone	m	0.500 – 2.00	UNIFORM	—
Number of Layers	—	1	CONSTANT	—
Saturated Hydraulic Conductivity	cm/hr	1.0 – 150	UNIFORM	—
Unsaturated Zone Porosity	—	0.250 – 0.500	UNIFORM	—
UNSATURATED ZONE FUNCTION VARIABLES				
ALFA Coefficient	1/cm	0.005 – 0.145	UNIFORM	(a)
Residual Water Content	—	0.034 – 0.100	UNIFORM	(b)
Van Genuchten Exponent	—	1.09 – 2.68	UNIFORM	(a)
UNSATURATED ZONE TRANSPORT VARIABLES				
Bulk Density of Soil for Layer	g/cc	1.25 – 1.76	UNIFORM	(c)
Longitudinal Dispersivity of Layer	m	—	DERIVED	(d)
Percent Organic Matter	—	0.180 – 1.30	UNIFORM	(e)
Thickness of Layer	m	0.500 – 2.00	UNIFORM	(a)

NOTES:

(a) Literature values obtained from Multimed User's Manual (1), Table 6–5, for sandy loam.

(b) Literature values obtained from Multimed User's Manual (1), Table 6–4, for sandy loam.

(c) Literature values obtained from Multimed User's Manual (1), Table 6–8, for sandy loam.

(d) Derived values obtained from the following calculation:
$av = 0.02 + 0.022L$,
where av = longitudinal dispersivity (unsaturated flow in the vertical direction)
L = depth of the unsaturated zone = 1 m

(e) Literature values obtained from Multimed User's Manual (1), Table 6–7, for Group B soils.

Table 8
Summary of Mutilated Input Parameters Used in Modeling PAH
Leachate Flow and Transport Through the Saturated Zone
of the Columbia River to the Adjacent River
Monte Carlo Model of Steady-State Conditions

INPUT VARIABLE	UNITS	VALUE(S)	INPUT TYPE	COMMENTS
CHEMICAL-SPECIFIC VARIABLES				
Acid Catalyzed Hydrolysis Rate	l/M-yr	0	CONSTANT	(a)
Base Catalyzed Hydrolysis Rate	l/M-yr	0	CONSTANT	(a)
Biodegradation Coefficient (Sat. Zone)	l/yr	0	CONSTANT	(a)
Dissolved Phase Decay Coefficient	l/yr	0	CONSTANT	(a)
Distribution Coefficient, Kd	—	—	DERIVED	(b)
Neutral Hydrolysis Rate Constant	l/yr	0	CONSTANT	(a)
Normalized Distribution Coefficient, Koc	ml/g	14.2 - 5,500,000	UNIFORM	(a)
Overall Chemical Decay Coefficient	l/yr	0	CONSTANT	(c)
Overall First-Order Decay Coefficient	l/yr	0	DERIVED	(d)
Reference Temperature	C	25	CONSTANT	(e)
Solid Phase Decay Coefficient	l/yr	0	CONSTANT	(a)
SOURCE-SPECIFIC VARIABLES				
Area of Eastern Source	sq.m.	10,000	CONSTANT	(f)
Infiltration Rate	m/yr	0.317 - 0.587	UNIFORM	(g)
Initial Concentration of Leachate	mg/L	100	CONSTANT	(h)
Length Scale of Source	m	100	DERIVED	(f)
Near Field Dilution	—	1	DERIVED	(g)
Recharge Rate	m/yr	0.308 - 0.744	UNIFORM	—
Source Decay Constant	l/yr	0	CONSTANT	(c)
Spread of Contaminant Source	m	16.7	DERIVED	(i)
Width Scale of Source	m	100	DERIVED	(f)
AQUIFER-SPECIFIC VARIABLES				
Angle off Centerline of Plume	degree	0	CONSTANT	(e)
Aquifer Porosity	—	0.26 - 0.57	DERIVED	(j)
Aquifer Thickness	m	4.57 - 6.10	UNIFORM	—
Bulk Density	g/cc	1.25 - 1.76	UNIFORM	(k)
Distance to Receptor, Xr	m	244	CONSTANT	(l)
Groundwater Seepage Velocity	m/yr	—	DERIVED	—
Hydraulic Conductivity	m/yr	142 - 3,780	UNIFORM	—
Hydraulic Gradient	—	0.0059 - 0.0068	UNIFORM	—
Longitudinal Dispersivity	m	24.4	CONSTANT	(m)
Mixing Zone Depth	m	—	DERIVED	—
Organic Carbon Content (Fraction), foc	—	0.0010 - 0.0076	UNIFORM	(n)
Particle Diameter	cm	0.0004 - 0.2000	UNIFORM	(o)
Retardation Coefficient	—	—	DERIVED	—
Temperature of Aquifer	C	16 - 25	UNIFORM	(e)
Transverse Dispersivity	m	8.13	CONSTANT	(m)
Vertical Dispersivity	m	1.37	CONSTANT	(m)
pH	—	6.00 - 9.00	CONSTANT	(e)

NOTES FOR TABLE 8:

(a) Literature values obtained from Aquatic Fate Process Data for Organic Priority Pollutants (4).

(b) Distribution coefficient was derived from the following equation:
Kd = Koc * foc,
where Koc = normalized distribution coefficient
Foc = organic carbon content (fraction)

(c) Conservative input value assumed.

(d) Value will be zero since it is derived from solid and dissolved phase coefficients, which themselves were assigned a value of zero.

(e) Assumed value(s).

(f) Area was designated as in Figure 1. Model assumed area is square, approximated area at 10,000 sq.m., with length = width = 100 m.

(g) Infiltration rates selected for model represents the minimum and maximum values derived from the Hydrological Evaluation of Landfill Performance (HELP) model.

(h) Assumed value.

(i) Spread of gaussian contaminant source = width of source/6.

(j) Porosity values represent range from fine sand to clay - Table 6-3, Multimed User's Manual (1).

(k) Literature values obtained from Multimed User's Manual (1), Table 6-8, for sandy loam.

(l) Determined from Figure 1.

(m) Longitudinal Dispersivity, aL = 0.1*Xr
Transverse Dispersivity = aL/3
Vertical Dispersivity = 0.056*aL

(n) No site-specific foc data available. Input value range obtained from Multimed User's Manual (1), Table 6-7, for Group B soils using the following equation:
foc = fom/172.4.

(o) Particle diameter range assumed for particle types ranging from fine silt to coarse gravel, given in Table 6-10 of the Multimed User's Manual (1).

Table 9
Parameters Used for Derivation of Soil Cleanup Goals

PARAMETER	DEFINITION
C_{awqc}	River concentration of a contaminant, equal to the appropriate AWQC.
DAF	Dilution-attenuation factor derived from Multimed as the ratio between the initial leachate concentration at the source and the modeled downgradient groundwater concentration at the receptor.
RM	River mixing (dilution) factor for contaminants in the river.
D_d	Soil-water equilibrium partitioning coefficient used for deriving interim soil cleanup goals from steady-state modeling.
C_i	Initial contaminant leachate concentration at source.
C_f	Final downgradient groundwater concentration at receptor location.
C_{gw}	Contaminant concentration in groundwater at point of discharge into river, back-calculated from river concentration, C_{wqc}.
C_{std}	Contaminant concentration in groundwater at monitoring well MW-102, equal to the appropriate groundwater performance standard.
C_l	Leachate concentration at source, back-calculated from downgradient target groundwater concentration (performance standard) at receptor location.
C_s	Soil concentration corresponding to interim soil cleanup goal.

River Approach

The calculations for developing soil cleanup goals protective of the river are as follows:

(1) Initial leachate PAH concentrations (C_i) are modeled from the designated source area through the unsaturated and saturated zones to the point of groundwater discharge at the river. A groundwater concentration at this location (C_f) is output by the model.

(2) The following relationship is then used to calculate a DAF:

$$DAF = C_i/C_f \tag{4}$$

(3) Assuming the target river concentration to be Cawqc, the targeted PAH concentration in the groundwater at the point of discharge into the river (C_{gw}) can be calculated by multiplying with RM, or:

$$C_{gw} = C_{awqc}\ RM \tag{5}$$

(4) Multiplying C_{gw} by the derived DAF from the model gives the leachate concentration at the source, C_l, or:

$$C_l = C_{gw}\ DAF \tag{6}$$

(5) Finally, multiplication of C_l by the distribution coefficient (K_d) results in a soil concentration at the source corresponding to the soil cleanup goal. This partitioning is expressed as the following:

$$C_s = C_l\ K_d \tag{7}$$

Soil Cleanup Goals for Total PAHs

The calculation for developing soil cleanup goals for total PAHs that are protective of the groundwater at monitoring well location MW-102 and the river is as follows:

(1) The leachate concentration of total PAHs (C_{lTPAH}) at each source is calculated in the same manner as follows:

For protection of groundwater at MW-102,

$$C_{lTPAH} = C_{std}DAF \tag{8}$$

For protection of the river,

$$C_{lTPAH} = C_{awqc}*RM*DAF \tag{9}$$

Since the MCLs and DWELs for each PAH are different, the lowest groundwater performance standard (0.0001 mg/L—proposed MCL for benzo(a)anthracene) is being used for totals PAHs as a conservative approach.

(2) Since the calculation of an soil cleanup goal for total PAHs (C_{sTPAH}) must take into account the K_d of each PAH (K_dPAH) as well as the percent distribution of each individual PAH ($\%D_{PAH}$) across the area of interest, the following assumptions can be made regarding the derivation of the soil cleanup goal.

For each PAH:

$$C_{lPAH} = C_{sPAH}/K_{dPAH} \tag{10}$$

where:

$$C_{sPAH} = C_{sTPAH}*\%D_{PAH} \tag{11}$$

Substitution of Equation (11) into Equation (10) yields the following relationship:

$$C_{lPAH} = (C_{sTPAH}*\%D_{PAH})/K_{dPAH} \tag{12}$$

For total PAHs, Equation (12) becomes:

$$C_{lTPAH} = \Sigma\ [(C_{sTPAH}*\%D_{PAH})/K_{dPAH}] \tag{13}$$

By moving C_{sTPAH} outside of the summation and rearranging, the following expression for the calculation of an soil cleanup goal for total PAHs is obtained:

$$C_{sTPAH} = C_{lTPAH}\ \Sigma(K_{dPAH}/\%D_{PAH}) \tag{14}$$

Table 10 presents a summary of the mean percent distribution of each PAH in soil at the site (%D), the distribution coefficient (K_d) of each PAH, and the adjusted distribution coefficient obtained for each PAH by dividing each K_d value by the corresponding %D.

RESULTS

Dilution-Attenuation Factors

Table 11 presents a summary of the dilution-attenuation factors (DAFs) that were derived from the final downgradient groundwater concentrations estimated at two receptor locations (MW-102 and the river) by the Multimed simulations of steady-state flow and transport from the source areas of the site, through the saturated and unsaturated zones. Table 11 shows that two DAFs were determined for each receptor location. One DAF was derived based on the results of a deterministic model, the other was derived based on the 95th percentile results of a Monte Carlo model of 500 iterative simulations.

Table 10
Summary of Distribution Coefficients
for Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbon	Mean Percent Distribution (%D) (1) (%)	Distribution Coefficient (Kd) (cm3/g)	Adjusted Kd Value (Kd') (2) (cm3/g)
Benzo(a)anthracene	6.33	6900	109,005
Benzo(a)pyrene	5.33	27500	515,947
Benzo(b)fluoranthene	10.0	2750	27,500
Benzo(k)fluoranthene	9.72	2750	28,292
Chrysene	7.66	1000	13,055
Dibenzo(a,h)anthracene	1.55	16500	1,064,516
Indeno(1,2,3-cd)pyrene	3.01	8000	265,781
Acenaphthene	2.96	23	777
Acenaphthylene	1.45	12.5	862
Anthracene	5.75	70	1,217
Benzo(g,h,i)perylene	2.97	8000	269,360
Fluoranthene	15.6	190	1,218
Fluorene	3.23	36.5	1,130
Naphthalene	2.74	4.7	172
Phenanthrene	9.83	70	712
Pyrene	11.8	190	1,610
		Sum Kd' = 2,301,155	

NOTES:
(1) %D for each PAH = (mean PAH conc./total mean PAH conc.)*100%
(2) Kd' = Kd/[(%D)/100]

The groundwater concentration of all PAHs estimated at receptor location MW-102 by the deterministic and Monte Carlo simulations of steady-state conditions were 8.38 mg/L and 2.23 mg/L, respectively. Since the original leachate concentration was arbitrarily assumed as 100 mg/L (for ease of presentation), the corresponding DAFs derived from the results of the deterministic and Monte Carlo modeling efforts to receptor location MW-102 are 11.9 and 45, respectively.

The groundwater concentration of all PAHs estimated at the point of groundwater discharge to the river by the deterministic and Monte Carlo simulations of steady-state conditions were 8.52 mg/L and 10.2 mg/L, respectively. Since the original leachate concentration was 100 mg/L, the corresponding DAFs derived from the results of the deterministic and Monte Carlo modeling efforts to the river are 11.7 and 9.8, respectively.

Soil Cleanup Goals

The DAFs derived and summarized in Table 11 were used to calculate soil cleanup goals for the site that are protective of: (1) the groundwater at monitoring well MW-102, (2) humans consuming aquatic organisms from the river and (3) marine organisms in the river. These soil cleanup goals are presented in Table 11.

Table 12 shows that the soil cleanup goals for total PAHs in Area A, derived from the results of the deterministic and Monte Carlo simulations, for protection of the humans consuming groundwater at the receptor well location were 2,738 mg/kg and 10,355 mg/kg, respectively. The soil cleanup goals for total PAHs in Area B, derived from the results of the deterministic and Monte Carlo simulations, for protection of the humans consuming river organisms were 41,866 mg/kg and 35,067 mg/kg, respectively. The soil cleanup goals for total PAHs in Area B, derived from the results of the deterministic and Monte Carlo simulations, for protection of river organisms were both greater than 1,000,000 ppm. Based on these soil cleanup goals and the existing PAH concentrations detected at the site, no soil remediation of PAHs would be necessary in either Area A or B.

CONCLUSION

Environmental fate and transport modeling of contaminants in the multimedia environment provides an alternative means of developing and establishing cleanup goals for potential source areas at hazardous waste sites. As was shown in this case, cleanup goals can be derived from modeling outputs that are protective of potential human and/or environmental receptors from contaminants as they become mobilized following release into the environment. The soil cleanup goals derived

Table 11
Summary of Dilution-Attenuation Factors from
Flow and Transport Models Through
Unsaturated and Saturated Zones
U.S. EPA Exposure Assessment Multimedia Model
Steady-State Conditions

Model Type for Steady-State Conditions	Assumed Initial Leachate Concentration for Each PAH at Source (1) (mg/L)	Modeled Final Groundwater Concentration for Each PAH at Receptor Location		Modeled Dilution-Attenuation Factor (2) for Each PAH	
		MW-102 (mg/L)	River (mg/L)	MW-102 (unitless)	River (unitless)
Deterministic Models of PAHs	100	8.38	8.52	11.9	11.7
Monte-Carlo Models of PAHs (3)	100	2.23	10.2	45	9.8

NOTES:
(1) Initial leachate concentration at source location is in the unsaturated zone. 100 mg/L was assumed for modeling presentation.
(2) Dilution-attenuation factors will be used for calculation of interim soil cleanup levels.
(3) Values presented for Monte-Carlo simulations represent the 95th percentile.

for this site were protective of both human and environmental receptors from PAHs originating from two source locations, with the most conservative soil cleanup goals being derived from both deterministic and Monte Carlo models for the protection of humans consuming groundwater as drinking water. These soil cleanup goals were 2,738 mg/kg and 10,355 mg/kg, respectively. The uncertainties associated with applying Multimed to the derivation of soil cleanup goals for this site are discussed in the following paragraphs.

In the deterministic models of steady-state conditions, literature values were used for chemical and physical properties of individual PAHs. These values may not be appropriate for the actual existing conditions at the site. Many of the literature values were obtained from laboratory conditions or field conditions different from those at the site. Many site-specific conditions may cause the chemical and physical properties and behaviors of the PAHs to deviate from values reported in the literature. In addition, the model evaluates chemicals separately. The behavior in the environment of chemicals which are constituents of mixtures, such as PAHs in creosote, may be different from their behaviors if these chemicals were present and interacting individually with the environment.

The Monte Carlo model of steady-state conditions assumes a constant, nondecaying source of large area and sufficient chemical mass to force the modeled system into steady-state conditions and equilibrium such that a constant downgradient groundwater PAH concentration is maintained at all times. In reality, however, the source strength may decay over time as PAHs migrate away (downgradient) from the source or degrade naturally.

An uncertainty associated with the Monte Carlo mode exists in the random generation of values from a specified distribution. It is uncertain whether the model considers interdependencies that may exist between or among many of the input variables. For example, Koc values may, in reality, change with the changing pH of a system. This variable is probably ignored by the model, especially when Koc values were entered as constant input.

Another consideration for uncertainty also exists in Monte Carlo simulations. Since there was a very limited base of site-specific data for each input variable, the uniform probability distribution was best suited for the input variables because of the degree of uncertainty associated with them. Hydraulic conductivity, for example, is estimated to follow a log-normal distribution and application of a uniform distribution may not be appropriate, but due to the lack of data for this parameter, it was the only option available.

Other overall uncertainties were associated with the use of the Multimed model for this site. These include: (1) the uncertainty resulting from a lack of sufficient aquifer-specific data for calibration of the model to actual conditions beneath the site; (2) the uncertainties that exist in parameter estimation from literature values, especially for values presented for a particular variable for different types or classifications of unsaturated and saturated zone materials (i.e., soils), none of which may adequately match the materials in the unsaturated and saturated zones at the site; (3) the uncertainty associated with the selection of a representative location and size of each source area; and (4) the uncertainty associated with source area geometry, since the model assumed that the geometry of each source area at this site was square, which in reality may not represent the actual geometry of the area. Selection of the area geometry will affect how the plume is modeled.

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Table 12
Summary of Interim Soil Cleanup Goals
Polycyclic Aromatic Hydrocarbons
Protective of Groundwater and the Adjacent River

Interim Soil Cleanup Goals					
Protective of Humans Consuming Groundwater from Well MW-102 (mg/kg)		Protective of Humans Consuming Aquatic Organisms from River (mg/kg)		Protective of Marine Organisms in River (mg/kg)	
Deterministic Model	Monte-Carlo Model (1)	Deterministic Model	Monte-Carlo Model (1)	Deterministic Model	Monte-Carlo Model (1)
2,738	10,355	41,866	35,067	403,852,702	338,269,785

NOTES:
(1) Interim soil cleanup goals presented for the Monte-Carlo model represent the 95th percentile.